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ON

SYNTHESIS OF POLYACRYLIC ACID BASED PRESSURE SENSITIVE ADHESIVES

FOR THE PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE OF
MASTER OF ENGINEERING

Submitted by:
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NEW DELHI
2003

ACKNOWLEDGEMENT

The project work mentioned in this report, is the result of commutative efforts over a period of six months, in course of which, I have received intellectual support from various sources. It is my pleasure to express my profound sense of gratitude to all those who have contributed richly to this project and has been highly instrumental in making this a success.

Although there is no novelty, no innovation to claim, but an attempt has been made by me to bring much more than my caliber.

I am highly indebted to **Prof. A. P. Gupta** (HOD, Department of Polymer science and Technology, Delhi College Of Engineering) for giving me an opportunity to work on this project. He has been an invaluable source of guidance and motivation at all stages of my work.

I express my thanks to **Dr. G. L. Verma** for his valuable suggestions time to time. Also my sincere regards to the **Dr. Poonam Kathuria, Dr. M. C. Gupta, Dr.Kunal Chandra and Dr. O.P. Bhardwaj.**

I am very much thankful to **Mr.M.L.Malhotra**(President,R&D,Jubilant Organosys Ltd.) who allowed me to pursue my six month project at R & D ,Sahibabad.

I take this opportunity to express my profound sense of gratitude to **Dr. Jagbir Singh** (DGM, R&D, Jubilant Organosys Ltd.) for providing me help, in spite of much engagement in his own work. I am grateful to him for his valuable guidance and supervision during whole of my project work. Without his supervision, it would have been extremely difficult for me to complete this work successfully.

My sincere thanks are also due to **Mr. R.K. Singh** to guide me continuously during my project. I am also thankful to all staff members of Jubilant Organosys Ltd. for their co-operation and help for solving difficulties, which I faced during this project work.

I am highly indebted to all of my family members to encourage me at all the stages. Without their support, it was impossible for me to achieve this.

Last, but not least, My special thanks should reserve to my colleagues who have directly or indirectly helped in my project.

Place: Jubilant Organosys Ltd., (JYOTI GUPTA)

CERTIFICATE

This is to certify that the project work entitled

"SYNTHESIS OF POLYACRYLIC ACID
BASED
PRESSURE SENSITIVE ADHESIVES"

Completed by
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ABSTRACT

The present thesis deals with the synthesis, characterization and performance testing of Polyacrylic acid based pressure sensitive adhesive. The main objective of the study was to synthesize Water Based Pressure Sensitive Adhesive for labels and tapes applications.

The pressure sensitive adhesives were synthesized by replacing conventionally used polyvinyl alcohol and hydroxyethyl cellulose as protective colloids with polyacrylic acid via emulsion polymerization technique. In order to optimize the performance characteristics of the pressure sensitive adhesive, the effect of different variables such as monomer, plasticizer, tackifier resin, monomer ratios with tackifier, polyacrylic acid concentrations and tackifier concentrations were studied.

Different properties were tested including solid content, pH, viscosity, mechanical stability and film observation. Loop tack tester, peel tester & cohesion tester were used to determine the tack, peel strength, and shear strength respectively of synthesized pressure sensitive adhesives.

Polyacrylic acid in the pressure sensitive adhesive is compatible and gives the desired values of shear strength and peel strength. Polyacrylic acid as protective colloid in the synthesized pressure sensitive adhesive improves the storage stability of the emulsion.

INDEX

i. Certificate
ii. Abstract
1. INTRODUCTION AND LITERATURE REVIEW
  1.1 Introduction 1
  1.2 Pressure sensitive adhesives 2
  1.3 Classification of PSAs 3
    1.3.1 Solvent Based Adhesives 3
    1.3.2 Hot Melt Adhesives 4
    1.3.3 Water Based Adhesives 4
  1.4 Pressure sensitive tapes and labels 7
  1.5 Emulsion Polymerization 8
  1.6 Mechanism 8
  1.7 Components of Emulsion Polymerization 11
    1.7.1 Monomers 11
    1.7.2 Water 12
    1.7.3 Initiators 12
    1.7.4 Surfactants 14
    1.7.5 Protective colloids 15
    1.7.6 Buffers 16
    1.7.7 Tackifier resins 16
  1.8 Performance Characteristics of PSAs 18
    1.8.1 Quick Stick 18
    1.8.2 Adhesion 19
    1.8.3 Cohesion 21
  1.9 Literature Review And Objective 23

2. EXPERIMENTAL DETAILS
  2.1 Preparation of Polyacrylic acid 32
  2.2 Preparation of Emulsion 34
    2.2.1 Raw Materials 35
    2.2.2 Formulations 36
    2.2.3 Experimental Set-up 36
    2.2.4 Procedure 36
  2.3 Analysis and Testing 37
    2.3.1 Solid content 37
    2.3.2 Viscosity 37
    2.3.3 Film observation 37
    2.3.4 Particle Size Distribution 38
    2.3.5 Free monomer concentration 38
    2.3.6 Mechanical stability 38
    2.3.5 Tack Test 40
    2.3.6 Peel Test 40
    2.3.7 Shear Test 40

3. RESULTS AND DISCUSSIONS
    3.1 Physical properties 41
    3.2 Stability 42
    3.3 Molecular weight determination 43
    3.4 Particle size distribution 44
    3.5 Effect of Plasticizer 45
    3.6 Effect of Polyacrylic acid 45
    3.7 Effect of Tackifier 46
    3.8 Effect of Tackifier concentration 47
    3.9 Effect of Monomer ratios with tackifier 47

4. CONCLUSION 56
5. REFERENCES 57

CHAPTER 1

INTRODUCTION
AND
LITERATURE
REVIEW

"Great books convey great thoughts,
Thoughts are the generator of new ideas."
- N. PAUL

1.1 INTRODUCTION

Adhesives are social substances used to unite materials. These were utilized in a sophisticated manner even in ancient times. The example appears in Carvings in Thebes dating back 3300 years depict the gluing of a thin piece of veneer to what appears to be a plank of sycamore . The glue pot and brush are shown . The Egyptians utilized gum Arabic from the Acacia tree, egg, glue, semi-liquid balsams, and resins from tree (10).

Rubber based pressure-sensitive adhesives were invented by Dr. Horace Day in 1845. Initially proposed for surgical use, they were used solely for that purpose for many years. With the advent of World War II, pressure sensitive adhesives became popular in many industries; they were even more favorably received in the post war year's (4).

Pressure sensitive adhesives (PSAs) are capable of holding together objects when the surfaces are brought into contact under briefly applied pressure at room temperature. Widely used pressure sensitive adhesives are water based, as these are not only cheap but also environmental friendly.

The suitability of polyacrylates for water based pressure sensitive adhesives was recognized as early as 1928. Polyacrylates found extensive use for pressure sensitive adhesives only in the 1950s and attained their importance in the 1960s. Polyacrylates possess some inherent properties that are superior to many other polymers used for pressure sensitive adhesives. Polymerization of acrylics is relatively easy and does not require high temperature or pressure (6).

Acrylics are modified with many other secondary comonomers to vary adhesive properties. These comonomers include vinyl acetate, vinyl pyrollidone, ethylene glycol, dimethylene acrylate etc. with high Tg. Sometimes multifunctional monomers are also used, which affect the wetting properties and provide cross linking sites(23).

The production of vinyl acetate - acrylate copolymers are industrially important because of their low cost, ease of production and wide applications. These are used in paints, adhesives, coatings, laminates etc. These can be tailor made according to final properties required by bulk, solution, suspension or emulsion polymerization techniques, using either a batch, semi-batch or continuous process. For adhesives the monomer ratio determines the final properties of the adhesive i.e. tack, peel strength & shear strength. High T_g monomer improves the cohesive strength whereas low T_g monomer enhances the and peel by introducing elasticity(19).

Pressure sensitive adhesives have quite important role in different areas of applications like packaging, hospital/first aid, office/graphic arts, construction, corrosion protection, automotive, electrical and others. Tape is the largest area of application and Labels is the second largest area. Other than these pressure sensitive adhesives have their application in self adhesive floor tiles, for décor papers & fly papers, gloss lamination, disposable diapers and other personal hygiene products & temporary assemblies(19).

1.2 PRESSURE SENSITIVE ADHESIVES

In English, the term pressure sensitive adhesives i.e. adhesives that bond when pressure is applied, admits pressure as an indispensable condition for their function. According to definition, pressure sensitive adhesives are " which in dry form are aggressively and permanently tacky at room temperature and adhere without the need of more than finger or hand pressure, require no activation by water or heat"(11).

This makes them arguably the most convenient products available today from the end user's viewpoint. A survey by Business Trend Analysts quoted in June 1990 issue of Adhesive age that PSA grew from38% of total adhesives sales in U.S. in 1980 to 44.6% in 1988.The total demand for PSA was 2.55 million metric tons in 1999(26).

1.3 CLASSIFICATION OF PSAs

Pressure sensitive adhesives depending upon their constituents, application and settings can be classified into three broad categories :

1. Solvent based
2. Hot - melt
3. Water - based

1.3.1 SOLVENT BASED ADHESIVES

The three major components are an elastomer, which provides the elastic phase; the tackifier; and the carrier i.e. organic solvent. These are applied with solvent; solvent evaporates leaving behind solid on the surface(19).

The earliest pressure-sensitive adhesives used natural rubber tackified with wood rosin, or later, zinc oxide. With the advent of synthetic rubbers and other polymers, formulators have a very much larger range of elastomers at their disposal, including butyl rubber, styrene-butadiene rubber, polyisoprene, and the more recent thermoplastic rubbers, which are block copolymers of styrene with butadiene or isoprene, as well as acrylic polymers. Tackifying resins include wood rosin derivatives and hydrocarbon resins(6).

Organic solvents used as carrier are undesirable because of cost, shortages, flammability, toxicity or tendency to pollute. As the price of solvents soared & as the environmental opposition to use of solvents increased, water based and hot melt types made substantial inroads into the solvent based market. Nevertheless, the excellent wetting characteristics plus applicability at low temperature and high coverage will enable them to retain an important role(10).

1.3.2 HOT MELT ADHESIVES

Hot melt adhesives are 100% solids at temperature below 79^{0}C. As temperature further increases the material rapidly melts to low viscosity fluid that can be easily applied. The major components of Hot-melt adhesives are polymer and diluent. Pressure sensitive hot melt adhesive is tacky to touch and can be bonded by the application of pressure alone.

The major differences between solvent based and hot melt pressure sensitive adhesive is that with hot melts the viscosity can no longer be controlled with solvents and must, instead, be controlled either by temperature or by formulating.

Hot-melt adhesives are used to bond all types of substrates, including metals, glass, plastics, ceramics, rubbers and wood.

Hot melt adhesives deals with high equipment cost, difficulty in cleaning, may undergo thermal degradation, can melt substrate and difficult to package. Alongwith these, they have very fast setting, no solvent waste and are environmentally acceptable(6).

1.3.3 WATER BASED ADHESIVES

Water based adhesives are made from materials that can be dispersed or dissolved in water alone .A dispersion usually consists of at least two monomers, one of high T_g and other with low T_g value and ratio of two will determine the final properties i.e. tack, peel strength and shear strength of the adhesive(19).

In recent years, exposure to organic solvents has been increasily controlled by the federal regulations. Therefore it is advantageous to use water-base rather than organic-solvent base adhesives. The use of water as a solvent results in lower cost, non-inflammability, and lower toxicity.

Water-base adhesives have fairly good organic solvent resistance. However, moisture resistance is usually poor (10).

Many adhesives today are made from latex i.e. rubber dispersion. In addition to natural rubber, the synthetic latices include styrene-butadiene, nitrile and chloroprene emulsion polymer synthetic rubbers; also vinyl acetate, acrylic, methacrylic, vinyl chloride, vinylidene chloride and styrene emulsion polymer synthetic resins. Synthetic latex is based on an aqueous dispersion of polymers obtained by emulsion polymerization. Each particle is separated or protected from the adjacent particle by a layer of emulsifier or protective colloid(12).

The rigid bonding applications include appliances, housewares, machinery, and electronics. Nonrigid bonding applications include fabrics, shoes, filters, and rugs. The largest application is in packaging(19).

The synthetic water based adhesives are divided into early synthetic (developed during the years 1935 to 1960) and new synthetics (developed since 1960). The demand for the natural water base adhesives in 1990 was approximately the same as the demand for the synthetics. However, by the mid-1990s the demand for synthetics outweighed that for the natural water base adhesives.

Polyvinyl acetate and its copolymers come in the category of early synthetics. These are the most widely used resins in water dispersions. These adhesives are the basis for common, household white glues. Setting is accomplished by the removal of water due to evaporation or absorption into substrate. These adhesives have poor weather, moisture, and solvent resistance but withstand grease, oil, and petroleum fuels. Additional properties are high initial tack, almost invisible bond lines, good biodegradation resistance, poor resistance to creep under load, and low cost. Applications include bonding to paper, plastics, metal foil, cloth and wood(19).

Table 1.1 Advantages and disadvantages of Pressure- Sensitive Adhesives

Solvent based	Hot melt	Water based
	ADVANTAGES	
Quick drying	Very fast setting	Easy cleaning
Good adhesion to non-polar substrates	No solvent waste	Good adhesion to polar substrates
Good key on certain plastics	Environmentally acceptable	Good heat and aging resistance
Versatile	100% active	Environmentally acceptable
		High solids
		Ready to use
	DISADVANTAGES	
	High equipment cost	
Flammability	Requires heat	Slow drying
Toxicity	Thermal degradation	Requires heat to dry
Relatively low solids	Difficult to clean	Poor on non polar substrates
Less easy to clean	Can melt substrate	
	Difficult to package	

1.4 PRESSURE SENSITIVE TAPES AND LABELS

PSAs are primarily used in tapes and labels, with tapes representing the largest area of application. PSA tapes have the following requirements:

- when the tape is unwound, the adhesive must remain on one side of the backing.
- the adhesive must not split or transfer to the other side.
- the unwinding force must be low.

Tapes can be classified by construction, function, application, or texture. The construction category includes fabric tapes, paper tapes, foil tapes, reinforced tapes, film tapes, non - woven tapes, foam tapes, two faced tapes and transfer tapes. The backing rather than the adhesive, is the distinguishing feature of this tape classification.

The function category includes masking, holding, sealing, reinforcing, protecting, bundling, stenciling, splicing, identifying, insulating, packaging, and mounting. The application category includes hospital and first aid tapes, office and graphic art tapes, building industry tapes, packaging and surface protection tapes, electrical tapes, automotive industry tapes, shoe industry tapes, appliance industry tapes, splicing tapes, and corrosion protection tapes.

The texture tapes category includes floor tiles, wall coverings, automobile wood- grained films, and decorative sheets.

Labels are the second largest application for PSAs. Specific characteristics that are important, and which differentiate labels from tapes, include backing material printability, flatness, ease of die – cutting , and release paper properties. The adhesive is applied to the release paper and allowed to dry. This material is then laminated to label stock(19).

1.5 EMULSION POLYMERIZATION

Synthesis of water based pressure sensitive adhesive involves free radical initiated emulsion polymerization. Emulsion polymerization is both one of the oldest and one of the newest forms of polymerization. This is the most widely used industrial technique. In emulsion polymerization, the, monomer is dispersed in the aqueous phase not as discrete particles but as a uniform emulsion. The emulsion is stabilized by surface-active agents (surfactants), protective colloids, and also by certain buffers(24).

Emulsion polymerization has certain advantages over other modes of polymerization.

- High molecular weights can be achieved at a high rate of polymerization.
- A small particle size may be obtained.

  Good heat transfer and high solids content may be achieved due to the low viscosity (high water content)
- Emulsions may be used direct in paints and adhesive applications(24).

1.6 MECHANISM

The mechanism for an emulsion polymerization of a water insoluble monomer has been qualitatively described by Harkins. It is assumed that the polymer is soluble in its own monomers. Harkin's theory describes reasonably well the emulsion polymerization mechanism of acrylic monomers(6).

Emulsifier molecules associate to form micelles. The highest concentration, wherein all the molecules are in dispersed state, or concentration beyond which only micelle formation is possible, is known as the 'critical micelle concentration' (cmc). We know that emulsifier molecules are made of two parts: a long non-polar hydrocarbon chain to which is attached a polar group. In micelle formation, the emulsifier molecules aggregate in such a way that the polar end of the molecules align themselves outward and the hydrocarbon ends come close to each other at the interior(24).

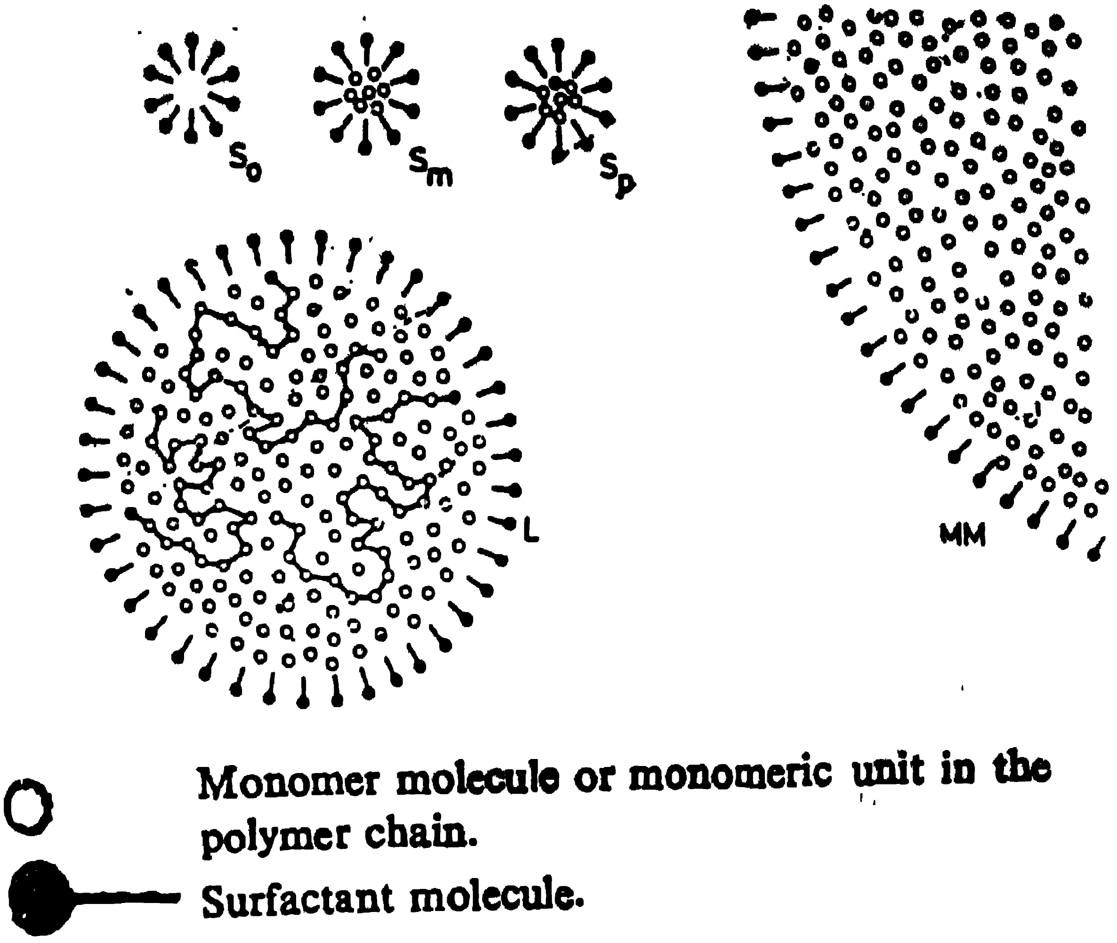


Figure 1.1 Schematic details of the various componenets present in an emulsion polymerization system. So, Sm, Sp, MM and L represent respectively the empty micelle, monomer-filled micelle, micelle with growing polymer chain, monomer droplets and latex particles containing monomer as well as growing polymer.

In emulsion polymerization technique, water soluble and monomer insoluble initiators are used, so there is hardly any initiator in the monomer droplet but an appreciable concentration of the initiator is found on the surface of micelle. Polymerization therefore starts at the surface layer of the micelle and proceeds inwards. At the same time, a small amount of monomer is solubilize in the micelles, and remaining monomer is dispersed in the small droplets. The locus of polymerization reaction is with in the micelles. As the polymer particle grows and the monomer is used up, the polymer absorbs more monomer that diffuses from the droplets through the aqueous phase to the micelles.

At the end of emulsion polymerization, we have fine particles of the polymer, stabilized by the emulsifier layer and dispersed uniformly in the aqueous phase. This milky white dispersion is called 'emulsion'.

Smith and Ewart have developed the quantitative theory of emulsion polymerization based on Harkin's description of the mechanism. Smith and Ewart show that the number of particles formed during the polymerization reaction is

$$N = \chi\, (\rho/\mu)^{2/5}(aS)^{3/5}$$

where

N =number of particles

ρ =rate of radical production

μ =rate of volume increase of a particle

a =area occupied by one soap molecule

S =total amount of soap present in the system

χ =a constant which varies between 0.37-0.53

But it has been shown that butyl acrylate emulsion polymerization does not obey the Smith-Ewart theory.

Butyl acrylate, is of course, a very important monomer for the pressure sensitive acrylic adhesive. The reasons for the deviation are slow termination and probably radical transfer out of particles(6).

1.7 COMPONENTS OF EMULSION POLYMERIZATION

Emulsion polymerization is a complex heterogeneous process. There are many components which can be present in an emulsion polymerization, such as monomer(s),surfactant(s), initiator, buffer, protective colloids, and water. All of these may affect the rate at which polymer is formed as well as the ultimate emulsion characteristics on which the application properties depend.

1.7.1 MONOMERS

Monomers are the building blocks in making polymers. The monomers used in the PSAs must possess the following properties in the combined state.

- Viscous properties to provide flow.
- The capability to dissipate energy during adhesion.
- Partial elastic behavior
- The tendency to resist excessive flow
- The ability to store bond rupture energy to provide peel and tack(2).

The generalized pressure sensitive acrylic copolymer composition is as follows:
Main monomer: 50-90%
Modifying monomer: 10-50%

In order to possess a low modulus of elasticity and an acceptable tack, the polymer must have a sufficiently low T_g. Of the commonly available monomers only 2 – Ethyl Hexyl Acrylate ($T_g = -70^0C$) and n-Butyl Acrylate ($T_g = -54^0C$) have sufficiently low T_g

Monomers of low T_g plasticize the adhesive, while monomers with high T_g increase the stiffness of the adhesive. Glass transition temperature is a useful indicator in choosing co-monomers, but its usefulness does not extend into fine adjustment of adhesive properties(6).

1.7.2 WATER

Water is a chief ingredient in emulsion polymerization. As the continuous phase, although inert, it acts to maintain a low viscosity and provides good heat transfer. In addition, it serves to isolate the polymerization loci. Termed compartmentalization, this is a particular advantage in emulsion polymerization. The water also acts as the medium of transfer of monomer from droplets to particles.

Natural water is the part of hydrological and geochemical cycle during which it comes in contact with the atmosphere, earth materials, living and decaying biological systems, and of course man-made pollutants. As a result, natural water has mineral (inorganic), organic and gas phase components. These contribute to the instability during emulsion polymerization. For this reason, most emulsion polymerization processes today use deionized water(9).

1.7.3 INITIATORS

A source of free radicals is needed for the water-bome emulsion polymerization. The free radicals can be produced by thermal decomposition of peroxy compounds like persulfate, or by redox reactions like the persulfate/bisulfite couple, or by γ-radiation.

Thermal initiators

The most frequently used water soluble thermal initiators are the salts of peroxydisulfate, i.e. persulfates.

The thermal decomposition yields sulfate radical anions:

$$S_2O_8^{2-} \longrightarrow 2SO_4^-$$
$$SO_4^- + H_2O \longrightarrow HSO_4^- + .OH$$
$$2.OH \longrightarrow H_20 + 1/2\ O_2$$

Ammonium or potassium persulfate is added to the emulsion and decomposed by raising the temperature to 50^0C or higher. About 0.5% of the initiator based on the monomer is sufficient to carry out the polymerization. In order to obtain the highest molecular weight possible, the initiator level should be kept low at the start of polymerization. Once the number of reaction loci is fixed, the level of persulfate has no effect on the polymerization rate.

Oil soluble thermal initiators such as benzoyl peroxide, 2,2-azobis(isobutyronitrile)are sometimes used. They partition preferentially into monomer- swollen particle and generate the free radical in that confined space(6).

Redox initiators

Various redox systems are used to initiate the polymerization of acrylic pressure sensitive emulsions.The combination of certain oxidizing and reducing agents will produce free radicals even at low temperatures. Common redox systems are : persulfate-bisulfite and persufate-hydrosulfite.

Persulfate- bisulfite system produce radicals according to the reaction:

$$S_2O_8^{2-} + HSO_3^- \longrightarrow SO_4^{2-} + SO_4^-\ . + HSO_3\,.$$

1.7.4 SURFACTANTS

Surfactants are a key formulation variable in emulsion polymerization. They can:

1. Act to stabilize the monomer droplets in an emulsion form.
2. Serve to solubilize monomer within surfactant micelle.
3. Stabilize the formed latex particles as well as the particles, which continue to grow during polymerization.
4. Act to solubilize polymer.
5. Serve as the site for the nucleation of particles.

Surfactants primarily determine the size and size distribution of the particles formed during emulsion polymerization. In general, polymerization carried out at or below the critical micelle concentration (cmc) will lead to the formation of particles with more uniform sizes. Surfactants are typically used in the range 1-6% by weight to monomer (lower concentrations for the anionic surfactants and the higher for the nonionic)(2).

A mixture of anionic and nonionic surfactants is generally used. Cationic surfactants are rarely used for polymerization of pressure sensitive acrylates. Adhesives containing surfactants may exhibit poor water resistance increased water absorbency, decreased tack and adhesion.

For the successful use of pressure sensitive acrylic emulsions, it important to eliminate the detrimental effects of the surfactants. One approach is the selection of the surfactants that have the least effect on the adhesive properties. Surface active agents that are compatible with the adhesive are least detrimental to the adhesive properties, because they are less likely to migrate to the adhesive surface. Obviously, the amount of surfactant used also has an effect on its capability to interfere with the adhesive properties(2).

The most commonly utilized nonionic surfactants for the emulsion polymerization are polyoxyethylenated alkylphenols, polyoxyethylenated straight chain alcohols, and polyoxyethylenated polyoxypropylene glycols(6).

1.7.5 PROTECTIVE COLLOIDS

In emulsion polymerization, a protective colloid, which is a water-soluble polymer, is usually used to increase the particle stability against coagulation. However, for particle size control, conventional surfactants are used. The most useful water-soluble polymers are most often non-ionic in character, and they add to the electrolyte stability as well as to the freeze-thaw stability of the latices.

In order for the water soluble polymer to work, a part of the chain must be anchored or strongly adsorbed on the particle surface, while the major part must be extended into the aqueous phase. This kind of stabilization is also known as steric stabilization. The protective colloids provide a hydrated shell around particles for steric stabilization(2).

Effective water soluble polymers used for this purpose have been Poly Vinyl Alcohol (PVAL) and cellulose derivatives, e.g.Hydroxyethyl Cellulose (HEC). PVAL continues to be favourite stabilizer for Poly Vinyl Acetate (PVAc) latex adheisves, while HEC is preferentially used for the architectural coatings. In both cases, grafting reactions are presumed to take place between the water soluble polymers and Vinyl acetate(VA) in solution to form pre-polymers, which subsequently collapse to form particles encapsulated by a hydrated polymer shell. This grafting process is more effective for PVAL and explains the high viscosity generally observed in this case. With HEC, grafting to VA is much less extensive and is accompanied by oxidative degradation of cellulose derivative (8).

1.7.6 BUFFERS

Buffers such as sodium bicarbonate and sodium acetate are often added to latex formulation to regulate the pH of the reacting system. Some monomers, such as acrylic esters, undergo hydrolysis reactions at elevated values of pH, while they remain stable at lower pH (7 or less).

The decomposition rate of initiators is also influenced by the pH; under acidic conditions decomposition of persulfate initiators are accelerated, which can lead to a reduction in the number of free radicals in the polymerizing system, with a resulting decrease in conversion.

These observations show that control of pH during polymerization is important, and that buffering helps regulate the pH. However, buffers are often salts and as such they can influence the colloidal stability of the latex and the particle size(2).

1.7.7 *TACKIFIER RESINS*

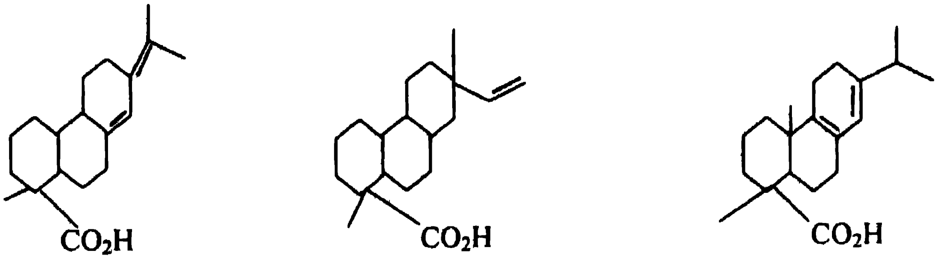
Pressure sensitive adhesives are viscoelastic materials. The viscous nature is defined by the low molecular weight resin. These are introduced to improve the tack. Tackifier resins should be compatible, low molecular weight and of higher glass transition temperature than that of the base polymer.

There are two major classes of tackifier resins. They are rosin derivatives and the hydrocarbon resins. The rosin derivative class consists of rosins, modified rosins, and various rosin derivatives; primarily rosin esters. The hydrocarbon resins class consists of low molecular weight polymers produced from a wide variety of monomers derived primarily from petrochemical sources.

Rosin is a thermoplastic acidic resin obtained from pine trees. There are three methods for obtaining rosin and the resulting product is named according to the process that was used. Gum rosin is obtained from extrudate, wood rosin is obtained from aged pine stumps and tall oil rosin is the third type of rosin obtained from tall oil which is the by-product of the paper industry.

The rosin acids are obtained from gum rosin, wood rosin or tall oil rosin. Rosins by itself are unsuited for use in modern adhesive systems because it is subject to oxidation and other reactions as well as crystallization. Because of this, most rosins for adhesive use have been subjected to one or more of a series of reactions to form modified rosins or rosin derivatives.

Among the more important reactions for the production of materials for use in adhesives are disproportionation, polymerization, hydrogenation, and esterification. The rosin esters are prepared by esterification of rosin acids with a variety of alcohols. In esterification, polyhydric alcohols (ethylene glycol; glycerol and pentaerythritol) are used to give rosins, which are stable and resistant to hydrolysis(14).



Neoabietic acid Pimaric acid Palustric acid

Examples of Rosin Acids

1.8 PERFORMANCE CHARACTERISTICS OF PSAs

The performance of a pressure-sensitive adhesive is dependent on three primary factors:

1. The "quick stick"
2. The adhesion
3. The cohesive strength

The proper balance of these properties is necessary in a good performing practical pressure-sensitive adhesive tapes and labels. Since adhesives are thermoplastic materials, temperature plays an important role in determining their physical properties. Tests are generally carried out at a standard temperature of 23°C but tests at low and high temperature are relevant to some applications.

These main adhesive properties depend on the composition of adhesive, state of the adhesive (pure or formulated), the coating technology (direct or transfer), the coating weight and face stock.

1.8.1 QUICK STICK

This property is the ability of the adhesive to immediately wet the surface to which it is applied under light finger pressure. The efficiency of this bonding process is related to the adhesive's ability to exhibit viscous flow.

The quick stick is frequently referred to as the "tack" of the adhesive. Tack of PSAs is not an exactly defined, physical characteristics; it may be defined as a separation energy. Tack is the resistance offered by an adhesive film to detachment from a substrate; it is the measure of the stretchiness of an adhesive, or the ability to form an instant bond when brought into low pressure contact with a substrate to which adhesive is to adhere.

The Pressure Sensitive Tape Council (PSTC) defines Quick Stick as " that which allows a pressure sensitive adhesive to adhere to surface under a very slight pressure." The American Society for Testing and Materials (ASTM) defines tack as the force required to separate an adherent and an adhesive at the surface shortly after they were brought rapidly into contact under a light pressure of short duration.

Tack is measured either by touch or quantitatively by means of a Loop Tack Tester, in which a loop of pressure sensitive adhesive coated substrate is brought in contact with test panel and the force required to immediately removing it, measured. The length of loop, application, removal speed, temperature and substrate are specified in test method.

"Rolling Ball" is among the earliest methods developed for measuring tack. It involves the use of a steel ball, which is rolled down an inclined ramp on to a strip of adhesive coated substrate. The distance the ball travels is recorded and shorter the travel length the higher the tack.

"Probe Tack" applies a standard probe to the adhesive surface and measures the force to remove it. The softness and thickness of the adhesive may also have some effect on the result. This is measured with the equipment called the Polyken Tack Tester(15).

1.8.2 ADHESION

This is the force required to peel away a pressure sensitive adhesive coated flexible material from a specified test surface under standard conditions. It is also known as peel force, peel adhesion or resistance to peel. Peel resistance data can yield more information about the adhesive character and its expected performance than other commonly used tests of pressure sensitive products: tack and creep resistance.

Most commonly used method is peel test. It involves a standard test plate, peeling off at a specific rate and angle it gives a measure of adhesive or cohesive strength, depending on the mode of failure.

Several geometrical combinations (Fig 1.2) are there to test the resistance to peel of pressure sensitive adhesive tapes. The basis for most standard tests of pressure sensitive tapes is ASTM D1000-60 or later versions. It is desired for tapes and removable labels, that no residue remains on the adherend i.e. adhesive failure is expected(7).

The most common substrate used is glass and stainless steel, but other surfaces may also be used. It is important that surfaces are cleaned according to standard test procedures. Peel adhesion test can be carried out on tensile tester(INSTRON) with an adhesion graph plotted on computer or chart recorder. A dedicated Adhesion Tester from ChemSultant can be employed. This instrument is specially designed for pressure sensitive adhesives.

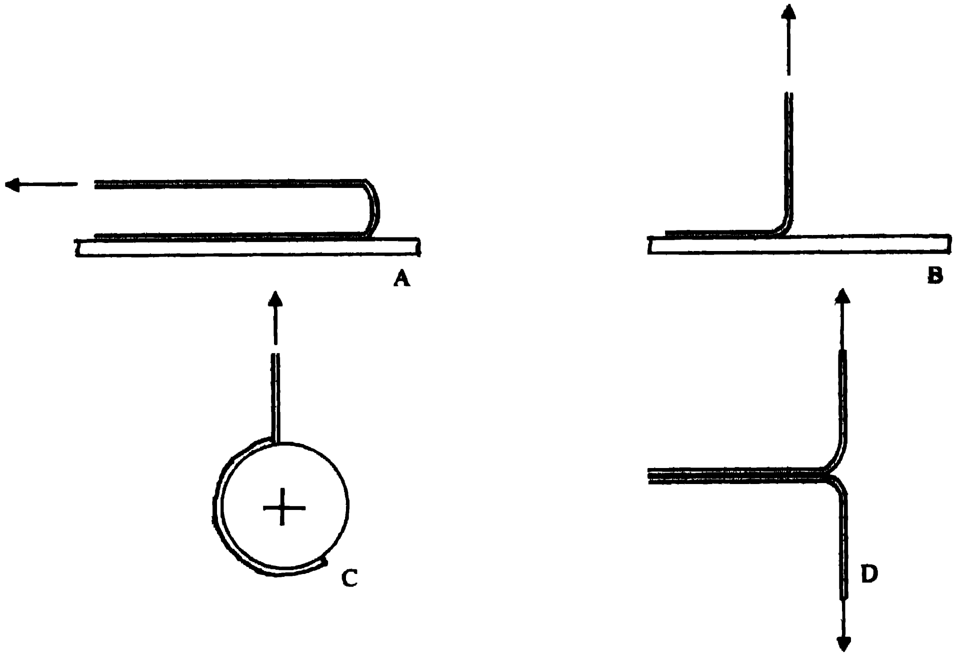


Figure1.2 Schematic diagram of various peel tests(a)180-degree peel test (b)90-degree peel(c) drum peel (tape unwind) (d) T - peel

ASTM D1000 contain 19 test methods and about half of these are of interest for all pressure sensitive tapes. The procedure of interest for peel testing include sample preparation, adhesion to steel plate, !80-degree peel test, drum adhesion, 90-degree peel test and other tests. T- peel test is described by ASTM D1876-61T and is used to check adhesive to adhesive bond.

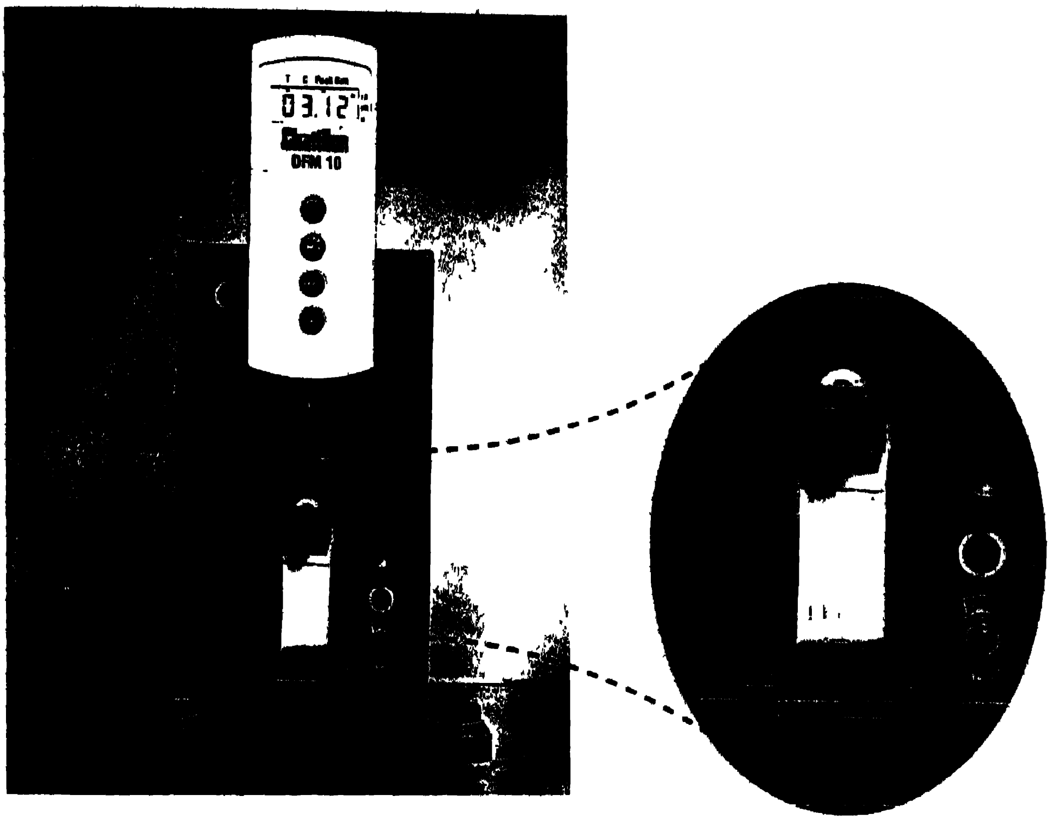
1.8.3 COHESION (SHEAR RESISTANCE)

A highly cohesive pressure sensitive adhesive is desirable for best performance or hold characteristics after application. The cohesion is a real measure of the internal structural resistance of the polymer. Generally, the mechanical properties of a polymer depend on its cohesion. It is also referred as resistance to creep of the adhesive.

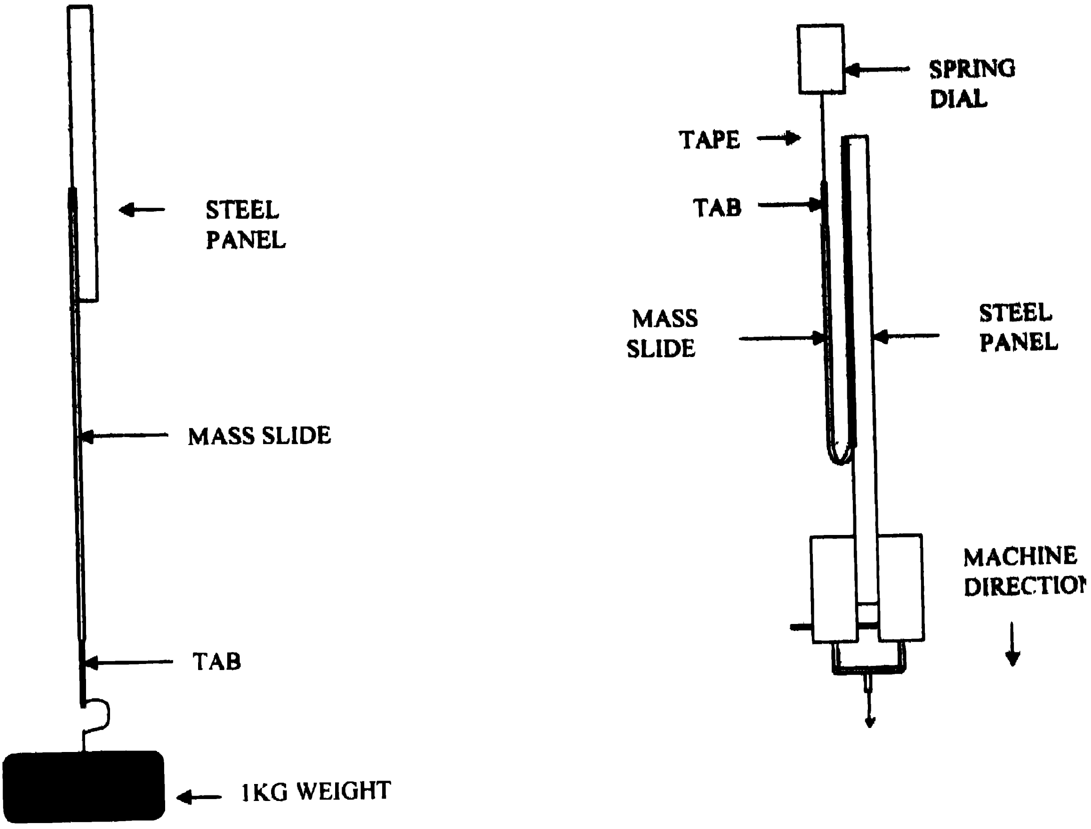
Shear resistance is measured as a force required to pull the pressure sensitive material parallel to the surface to which it was affixed with a definite pressure. The shear resistance may be measured statically or dynamically. Static Shear tests use a constant load at a longer test times; they generally show poor reproducibility and need very long measurement times. Dynamic shear tests measure the cohesion of the sample in a tensile tester under increasing load.

Shear tests are normally carried out in triplicate, and test equipment is available with up to 30 individual stations, with separate timers. Normally an angle of 20 from the vertical is employed, which prevents any peeling motion, ensuring that the only forces acting are parallel with the adhesive bond line(27).

Better results are obtained with hot shear tests, where cohesion of sample is measured at an elevated temperature. The temperature at which bond fails is taken as a characteristic value, is called as Shear Adhesion Failure Temperature (SAFT)(12).



(A)



(B) (C)

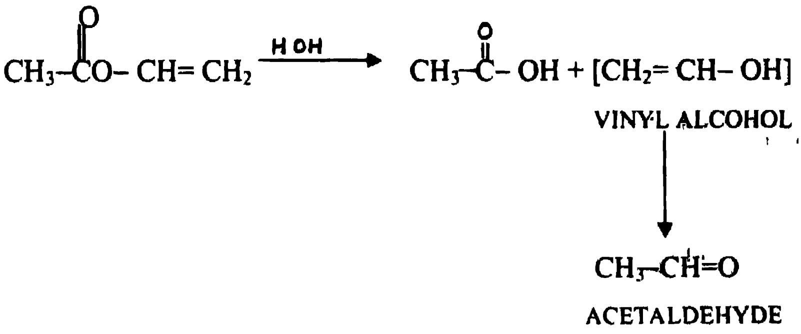
Figure 1.3 Presentation of various methods of testing (A) loop test (B) peel test (C) shear test.

1.9 LITERATURE REVIEW AND OBJECTIVE

The protective colloids widely and traditionally used in pressure sensitive adhesives are poly vinyl alcohol and hydroxyethyl cellulose. They can be used alone or in combination.

Polyvinyl alcohol

Vinyl alcohol, the monomer of polyvinyl alcohol, does not exist in the free state. Acetaldehyde, the keto form is more stable.



$$CH_3-\overset{O}{\overset{\|}{C}}O-CH=CH_2 \xrightarrow{HOH} CH_3-\overset{O}{\overset{\|}{C}}-OH + [\underset{\text{VINYL ALCOHOL}}{CH_2=CH-OH}]$$

$$\downarrow$$

$$\underset{\text{ACETALDEHYDE}}{CH_3-CH=O}$$

Hydrolysis of polymeric vinyl esters leads to stable form, poly vinyl alcohol.

$$[--CH_2CH(OCOCH_3)--]n \xrightarrow{HOH} n\,CH_3COOH + [--CH_2CH(OH)—]n$$

POLYVINYL ALCOHOL

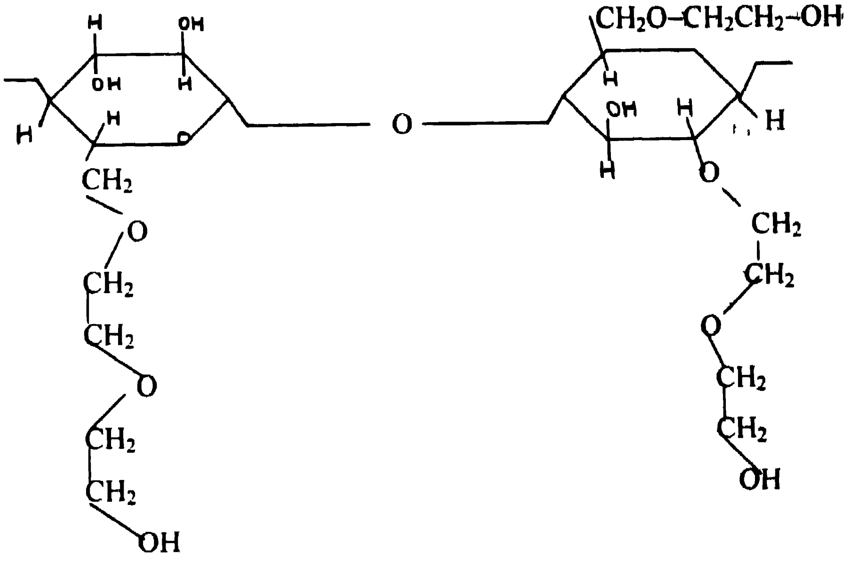
Polyvinyl alcohol is an important derivative of poly vinyl acetate. Hydrolysis of polyvinyl acetate using CH_3OH may be partial or total and various grades of polyvinyl alcohol are produced, each differing in extent of hydrolysis. Hydrolysis is carried out in presence of acidic & basic catalysts.

Partially hydrolysed (70-98%) polyvinyl alcohol of molecular weight 2000- 100,000 is used as an emulsion protective colloid, tend to be softer and more easily dissolved in water than fully hydrolysed material(13).

Hydroxy ethyl cellulose

Water soluble hydroxy ethyl cellulose is usually manufactured by the action of ethylene oxide on cellulose in the presence of alkali, in particular of caustic soda. The molecular weight of water soluble cellulose derivatives are probably between 50,000-500,000.

The structure of hydroxy ethyl cellulose is



STRUCTURE OF HYDOXY ETHYL CELLULOSE

Polyvinyl alcohol is used as an emulsifier and protective colloid in the emulsion polymerization of vinyl acetate and copolymers of vinyl acetate to form high-solids emulsions with outstanding stability and excellent adhesive properties. It can be used to control particle size and particle size distribution(8).

Polyvinyl alcohol and Hydroxyethyl Cellulose both function as nonionic emulsifiers and protective colloids in the preparation of oil-in-water type emulsions and dispersions. They also retards creaming and settling by acting as a viscosity builder in the continuous phase.

The protective colloid property does not appear to be affected by molecular weight, while the viscosity-building effect increases with increasing molecular weight. The concentration of polyvinylalcohol used to produce stable emulsions or dispersions containing 30-50% of the dispersed phase is generally from 2-5%, based on the total weight of emulsion. Hydroxyethyl cellulose has been used for increased stability as well as for rheology control(9).

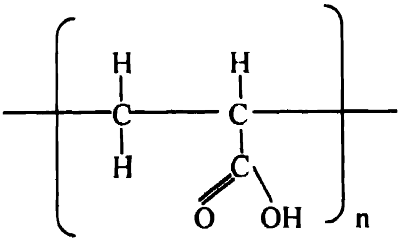
There are examples where latexes used in the pigmented systems are stabilized with water-soluble polymers of poly (acrylic acid), poly (methacrylic acid) or poly (isobutylene/maleic anhydride). The poly(acrylic acid)have its application in various fields(25) e.g.

Adhesives
Binders
Coatings
Desalination
Dispersants
Emulsion Paints
Films
Laminated structure
Thickeners
Water treatment

It was an idea to synthesize pressure sensitive adhesive using polyacrylic acid as a protective colloid in the emulsion and to observe its suitability for replacement/substitution of poly vinyl alcohol and hydroxy ethyl cellulose.

The compatibility of poly (acrylic acid) in pressure sensitive adhesive was observed from performance characteristics of synthesized pressure sensitive adhesives.

High molecular weight polyacrylic acid have been used successfully in many aqueous systems as thickeners for more than a quarter of a century. The general structure of these thickeners is shown in structure 1.



Structure 1

When dissolved in water in their native form, these polymer molecules adopt the relatively relaxed configuration shown in Figure 1.4.

Upon neutralization with a suitable base, the carboxylate groups ionize, and mutual ionic repulsion between these groups causes the molecule to adopt a greatly expanded configuration(Figure 1.5).

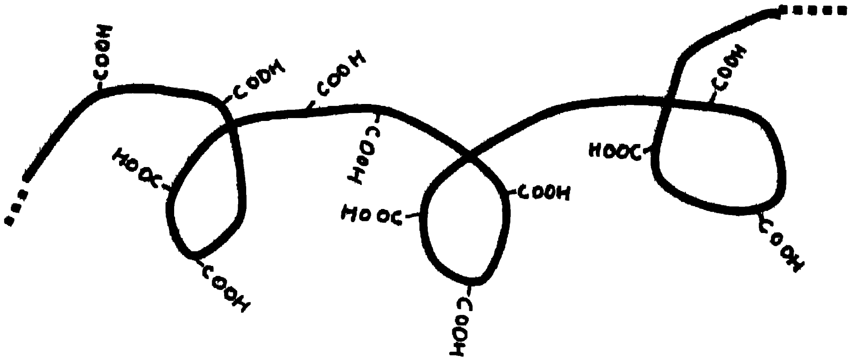


Figure 1.4 Schematic diagram of Poly acrylic acid in relaxed configuration

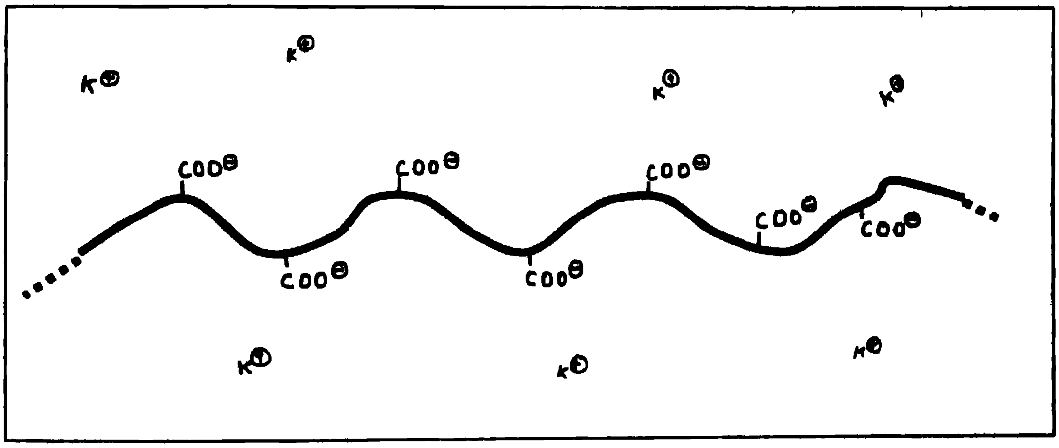


Figure 1.5 Schematic representation of stretched configuration of potassium salt of polyacrylic acid

Neutralization to pH 5 causes polyion expansion. Desired viscosity reaches between pH 5 and 10. Above pH 10 the effective increase in counterion concentration causes a successive reduction in the swelling of they polyelectrolyte molecules. Type shows viscoelastic characteristics, and type B displays plastic rheology(Figure 1.6). Polymer type A has a reported number average molecular weight of 4 million & polymer type B has a reported number average molecular weight of 500,000(22).

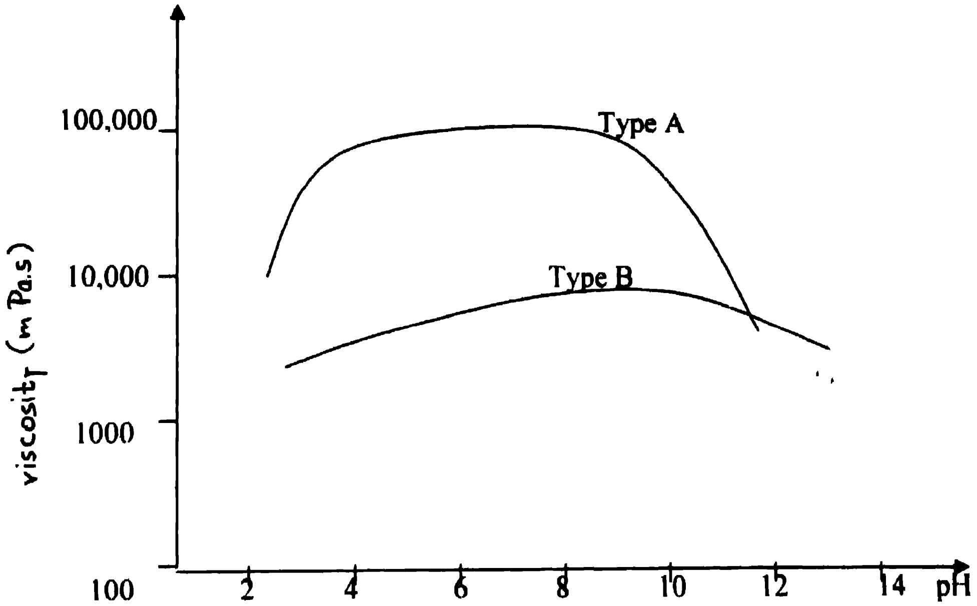


Figure 1.6 Variation of Brook Field Viscosity with pH

It is known that acrylic based pressure sensitive adhesive can be tackified to improve adhesion to non-polar substances such as polyolefins. However most of the commercially available tackifiers have low molecular weights as compared to adhesive polymer and their addition to the polymer lowers the shear properties. Tackification of pressure sensitive adhesive improves room temperature performance and in most cases, the

performance of tackified adhesive is less than that of the non-tackified pressure sensitive adhesive. Performance characteristics would thus appear to depend on selection of tackifier, their functional group and concentrations (3).

Numerous approaches have been used to produce resin emulsions. US Patent 5,623,011 to Bernard describes the physical mixing of (a) emulsion polymer formed from alkyl acrylates, vinyl esters, diesters of di carboxylic acids, unsaturated carboxylic acids with (b) a tackifier having an acid number 30- 60 and softening point 50-70^{0}C.

In Japanese Patent J-51125472, a petroleum resin emulsion is obtained by polymerizing vinyl monomers in the presence of petroleum resins having softening point 40 – 160°C, average molecular weight of 300 – 3000. The resin emulsion produced is described as having fine particle sizes and ample stability and when cured, the films produced have excellent water resistance and gloss.

One approach is to dissolve the resin in a hydrocarbon solvent, combine the resin solution and water to form an emulsion, and strip the solvent. Invariably some residual hydrocarbon solvent remains in the finished emulsion whish is undesirable in certain applications. This has led to the development of solvent free dispersions(US Patent no.2,809,948)and emulsions(US Patent no.3,377,298) of petroleum resins.

In US Patent 5317055, a water based pressure sensitive adhesive is formulated by homogeneously incorporating the tackifying resin into the polymer matrix. The tackifying resin is dissolved into a solution of alkyl(meth)acrylate and (meth)acrylic acid monomers, prior to polymerization. To enhance the molecular weight of the resultant pressure sensitive adhesive the monomer/tackifier solution is emulsion polymerized in the absence of chain transfer agents, such as antioxidant additives, typically found in commercially available tackifiers.

Further, it is an objective to incorporate the tackifying resin free of chain transfer agents, such as antioxidants in the polymer matrix, including monomers vinyl acetate and butyl acrylate and observe the effect on performance properties.

The present work comprises:

1. Synthesis of Poly(acrylic acid)
2. Synthesis of poly (acrylic acid) based pressure sensitive adhesive.
3. Study the effect of change of

- Plasticizer.
- Poly(acrylic acid) concentrations.
- Tackifier.
- Tackifier concentrations.
- Monomer ratios with tackifier.

CHAPTER-2

EXPERIMENTAL DETAILS

" As to knowledge connected with books, there is a need for a step to be taken before you can fairly reach upon any result "

-WILLIUM COBBETT

2.1 PREPARATION OF POLYACRYLIC ACID

The poly(acrylic acid) used for the synthesis of emulsion was prepared in the lab itself, using the following raw materials and procedure. It was neutralized and checked for its solid content, pH and viscosity before using.

RAW MATERIALS

DM water = 760.0 gm
Acrylic Acid = 34.0 gm
PPS + water = (0.025 + 1.0)gm [I -VII]
KOH = 17.0 gm
DM water = 68.0 gm

EXPERIMENTAL SET-UP

The experimental set –up consists of a 2 Lt. glass kettle with a four mouthed lid, fitted with condenser, stirrer. The kettle is placed in a water – bath to maintain the reaction temperature.

PROCEDURE

(i) DM water and acrylic acid were taken in the 2 Lt. Kettle.
(ii) The mixture was heated up to 70°C in 2½ hrs.
(iii) PPS[I] added to this and temperature was raised to 75°C slowly in 30 min.
(iv) PPS[II]added to this and temperature raised to 90°C in 60 min.
(v) PPS [III – VII] added at 1 hr interval keeping the temperature at 90°C.
(vi) Cooled down to 40°C.
(vii) KOH solution added to maintain the pH = 5.5 – 5.8.

(viii) The polyacrylic acid formed was analysed for its solid content and viscosity.

The solid content should vary from 6-7% and viscosity from 300-450 cp.

PROPERTIES OF POLYACRYLIC ACID

VISCOSITY = 440 cp
SOLID % = 7.33 %
pH =7.34

2.2 PREPARATION OF EMULSION

2.2.1 RAW MATERIALS

1. Vinyl Acetate Monomer; Jubilant Organosys Ltd., Gajraulla.

   Colorless, flammable liquid, initially pleasant odour that quickly becomes sharp and irritating, ($T_g = 30^oC$).
2. 2-Ethyl Hexyl Acrylate; Jubilant Organosys Ltd., Gajraulla.

   Colorless, flammable liquid with $T_g = -70^oC$.
3. Butyl Acrylate; Jubilant Organosys Ltd., Gajraulla.

   Clear, colorless liquid with fruity odour and $Tg = -54^oC$
4. Sodium Acetate anhydrous (82.03); Qualigens fine chemicals, Mumbai.

   It is used as buffer to control the pH of reacting system.
5. Fynol NXZ; Fine Organics, Mumbai.

   It is the defoamer added to avoid the formation of air bubbles in the emulsion.
6. Potassium Per Sulfate

   It is free radical initiator commonly used in emulsion polymerization.
7. Acrylic Acid; Atofina (earlier Elf AtoChem), France.

   It was used to prepare poly acrylic acid.
8. NOIGEN PA-40; DIA-ICHI Chemicals, Mumbai.

   Nonionic, oil soluble, wetting, dispersing and emulsifying agent. Its chemical nature is polyethoxy ether.
9. Tackifier Rosin (RB5); Dev Resins Pvt.Ltd.,H.P.

   Tackifier rosin used was glycerol ester (unstabilized),transparent and light reddish with acid no – 7.2, softening point – 85.
10. DeMineralized Water

    Demineralized water was used to avoid the effect of salts and other organic matter present in it.

2.2.2 FORMULATIONS

No of batches were taken and repeated to see the consistency. The batches different in composition have been shown here.

BATCH NO	PAA	VAM	2-EHA	BA	DBM	DOM	NXZ	SOD. ACE.	PA-40	GEO WET-5X	ROSIN	PPS
1	400	129.3	300	-	-	-	0.5	2.6	22.2	-	-	1.5
2	400	129.3	215	-	85	-	0.5	2.6	22.2	-	-	2.0
3	400	129.3	215	-	-	85	2.7	2.6	22.2	-	-	2.0
4	400	129.3	-	257	42.5	-	2.7	2.6	22.2	-	-	3.0
5	400	129.3	-	300	-	-	2.7	2.6	22.2	-	-	3.0
6	200	129.3	-	300	-	-	2.7	2.6	22.2	-	-	2.5
7	100	129.3	-	300	-	-	2.7	2.6	22.2	-	-	2.5
8	150	129.3	-	300	-	-	2.7	2.6	-	2.2	-	2.5
9	125	136.3	-	315	DAM-0.5	-	2.7	2.6	-	2.2	-	2.5
10	200	122	-	283	-	-	2.7	2.6	22.2	-	45	3.0
11	200	85.5	-	342	-	-	2.7	2.6	22.2	-	22.5	3.0
12	200	83	-	333	-	-	2.7	2.6	22.2	-	34	3.0
13	200	81	-	324	-	-	2.7	2.6	22.2	-	45	3.0
14	200	80	-	320	AA-4.5	-	2.7	2.6	22.2	-	45	3.0

Table 2.1 composition of different batches

Θ For Convenience, the quantities are shown in gms taken as the wt % of the whole batch.

2.2.3 *EXPERIMENTAL SET-UP*

The experimental set –up consists of a 2 Lt. glass kettle with a four mouthed lid, fitted with condenser, stirrer and monomer feeding funnel. The kettle is placed in a water – bath to maintain the reaction temperature.

2.2.4 *PROCEDURE*

(i) Required amount of polyacrylic acid and DM water were charged in kettle, stirrer started and bath temperature was increased from room temperature to reaction temperature (85^{0}C) over a period of one hour.

(ii) Monomer mixture was prepared along with monomer soluble surfactant.

(iii) Defoamer and buffer were added to the kettle in desired quantity at the same temperature.

(iv) A part of initiator solution was added and simultaneously monomer feeding was started.

(v) Feeding was continued at a constant rate for 5-1/2 hours, with 1/10th of remaining initiator solution.

(vi) After feeding, the reaction mixture was held at 90^{0}C inside the kettle for 2 hours.

(vii) Then it was cooled down to room temperature and discharged.

2.3 ANALYSIS AND TESTING

2.3.1 SOLID CONTENT

The percentage by weight of nonvolatile matter is called 'solid content'. Approximately 1.0 gm of sample was taken in pre weighed Al-foil, and then dried at 105^{0}C for 3 hrs. It can be calculated as

$$\% \text{ solid} = [(C - A) \div (B - A)] \times 100$$

where,

A = weight of Al-foil(gm)
B = weight of Al-foil with sample before drying(gm)
C = weight of Al-foil with sample after drying(gm)

2.3.2 VISCOSITY

The viscosity of emulsion was measured by using Brook Field Viscometer. The spindle numbers ranging from 1 to 7 were used according to the requirement, the speed and temperature were maintained 20 rpm and 30^{0}C respectively.

2.3.3 FILM OBSERVATION

A 100 μ film was casted on clear, dry glass plate using an applicator. The applicator has flat groove of 100 μ depth. The clarity, foam presence, and grits presence was checked in the film

2.3.4 PARTICLE SIZE DISTRIBUTION

JOYCE – LOEBL disc centrifuge was used to determine the particle size distribution of the emulsion. A relatively inexpensive system for a variety of materials with a photometer attached. The photometer is the detector for monitoring particle movement in the field by turbidity measurement with the time at a particular point on the transparent disk. The results obtained are a measure of the distribution of the particle sizes.

2.3.5 FREE MONOMER CONCENTRATION

Vinyl acetate contains unsaturation and consumes bromine and the same is taken as the basis for its content.

Weigh 10 gm sample accurately in 250 ml conical flask, add 50 ml of DM water and stir by means of a glass rod. Titrate against 0.1 N bromine solution until light pale yellow color persists for 30 seconds.

$$\% \text{ Free monomer} = (R*N*4.3)/W$$

where,

R= Bromine solution in ml required for titration

N= normality of bromine solution

W= weight of sample in gms.

2.3.6 MECHANICAL STABILITY

300 gm of latex sample placed in a waring and stirred at high speed (5000-8000 rpm) for 15 min. The latex is then filtered through a 200 mesh screen. No or at most only very little coagulum should remain on the filter. The test is repeated with 300 gm of the latex diluted with water to5% solids. A latex passing both test can be considered mechanically stable.

PERFORMANCE TESTING

The performance of the adhesive after its application can be determined by three important tests. These tests determine the extent of adhesion and cohesion of adhesive.

To do these tests the laminates of adhesive on PET(23μ) film are prepared. These are kept at room temperature for 24 hrs or more (dwell time). The one inch wide strips in longitudinal direction of adhesive application were cut with a cutter specified for it. These strips are used to measure different properties. The temperature was maintained at 23 ± 2^0C and relative humidity at 55 ± 5. The coating weight was maintained in the range 23 – 25 gm/m^2.

The coating weight was calculated by using formula

$$GSM = (W_2 - W_1) / C$$

W1 = 1 inch* 1 inch PET film weight

W2 = 1 inch * 1 inch coated PET film weight

C = $6.4516 * 10^{-4}$

The instruments used for tack, peel and shear tests were from ChemInstruments, fairfield, Ohio,USA. The instruments were manufactured to meet ASTM ,PSTC, TLMI, FINAT and AFERA standards.

During these tests the adhesive failure and cohesive failure was also observed. Adhesive failure results when adhesive remains on the film while cohesive failure occurs when adhesive gets transfer to the steel panel. These failure also supports the high tack and high shear for cohesive and adhesive failures respectively.

2.3.7 TACK TEST

The tack test was done by using 'Loop Tack Tester' in which a loop of pressure sensitive adhesive coated substrate was brought in contact with a test panel and the force required to immediately remove it, measured.

The length of loop, application / removal speed, temperature, substrate, and coating weight are factors influencing the results. The units are lb/25mm^2. This test is described by ASTM D 6195 – 97.

2.3.8 PEEL TEST

It is the measurement of adhesion. The adhesive coated substrate was made to adhere on the test panel. Load was applied by the hand roller weighing 2 Kg. The force required to peel off this from a test panel was measured. The rate of peeling off and peel angle were specified as 300mm / min and 180^0. The units for peel strength are in gm/25mm^2. This test for resistance to peel is described by ASTM D 3330 M.

2.3.9 SHEAR TEST

The basis of the test is that force is applied in a plane parallel to the bond line. The static shear was used. The load used was 1Kg and are of contact on test panel was 1 inch × 1 inch. An angle of 2^0 from vertical is employed which prevents any peeling motion. The load, angle, contact area, substrate dwell time and temperature influence the results. This test is described by ASTM D 3654 M.

CHAPTER-3

RESULTS AND DISCUSSIONS

" Better indeed is a knowledge than mech
Better than knowledge is meditation,
But better still is surrender to attachment to results,
Because these follows immediate peace. "
- SHRI KRISHNA

3.1 PHYSICAL PROPERTIES

The properties of the different batches studied were obtained as in the table given below.

Table 3.1 Physical Properties of various emulsions

BATCH NO	COLOR	SOLID%	VICOSITY (POISE)	PH	FILM OBSERVATION	MECHANICAL STABILITY
1A	Milky White	50.0	72	4 -6	Large grits, clear, no foams	Stable
2A	Milky White	52.75	61	4 – 6	Large grits, foam cells, clear	Stable
3A	Milky White	51.2	120	4 – 6	Small grits, hazy, waxy	Stable
4A	Milky White	55.3	181	4 - 6	Non-gritty, clear, No foams	Stable
5A	Milky White	59.0	160	4 – 6	Non-gritty, clear, No foams	Stable
6A	Milky White	53.00	135	4 -	Non- gritty, clear, no foams	Stable
7A	Milky White	50.0		4 - 6	Non-gritty, clear, No foams	Stable
8A	Milky White	48.49	80.5	4 – 6	Non-gritty, clear, No foams	Stable
9	GELLING OCCURED					
10C	Off white	50	93	4 – 6	Small-grits, micro foam, hazy	Stable
.11C	Off white	53.2	108	4 – 6	No foam and grits, Hazy.	Stable
12C	Off white	51.1	108	4 – 6	Negligible grits & foams, hazy	Stable
13C	Off white	52	96	4 – 6	Micro-grits, micro-foam, hazy	Stable
14C	Off white	51	139	4 – 6	Micro-grits, large-foams, hazy	Stable

The variation in properties can be discussed as follows:

The color of the emulsion varies from milky white to off white due to addition of the tackifier resin which is light yellow in color.

The viscosity depends upon the amount and type of initiator, surfactant, amount of protective colloid.

The viscosity of emulsion also depends upon feeding rate and temperature of the reaction.

The pH remains in the range specified for the acrylic pressure sensitive adhesives.

The grits presence in the initial batches shows that the poly(acrylic acid) is not compatible with VAM - 2EHA system.

The surfactant change does not give much desired properties thus the non-ionic, oil soluble surfactant was continued for further batches.

The alphabets 'A' and 'C' with the serial no. of batches show the adhesive failure and cohesive failure respectively.

The free monomer concentration of the emulsions was varying from 0.5 to 0.8 percent.

3.2 STABILITY

The stability of emulsion is improved by the use of protective colloids. Here the replacement of polyvinyl alcohol and hydroxy ethyl cellulose by poly(acrylic acid) is being done. Thus the mechanical stability and physical stability at 30^0C were studied.

The mechanical stability of all batches was observed with no coagulum formation, no phase separation and no viscosity change after stirring the emulsion at high speed(5000-8000 rpm) and keeping for one week

The physical stability of the emulsion was observed by measuring the viscosity. There was no appreciable change in viscosity after 2 - 3 months, but slight decrease in viscosity (10-15 %) was observed after six months.

The results were comparable with the emulsion formed with traditionally used protective colloids.

3.3 MOLECULAR WEIGHT DETERMINATION

The molecular weight of the emulsion can be determined by different methods. The common thing among all methods is to dissolve the dried emulsion in solvent. The emulsion synthesized was not soluble in Tetrahydrofuran, mainly used for the GPC method. Thus solubility in different solvents was studied. The solvents taken under consideration and their results after 24 hours are given below.

SOLVENT	SOLUBILITY
Methanol	Swelling
$CHCl_3$	Swelling
DMF	Swelling
Ethanol	Swelling
Acetone	Swelling
DMSO	Swelling
Toulene	Swelling
MEK	Swelling
Isopropanol	Swelling

Various combinations of solvents were also considered.

1. Toluene + MEK + I P ---------------- swelling after 24 hrs.
(40%) (40%) (20%)

2. Toluene + MEK ---------------- slightly soluble
(50%) (50%)

3. Toluene + MEK + Acetic acid ---------------- Insoluble with swelling
(49.5%) (49.5%) (1%)

This indicates that the emulsions formed are of very high molecular weight or there is formation of interpenetrating polymer networks. The emulsions soluble in the toluene and MEK mix were of tackified type while non-tackified were totally insoluble.

3.4 PARTICLE SIZE DISTRIBUTION

The particle size distribution of different emulsions is studied. As the graphs(G1 – G7) shows that the number average diameter of different samples are in the range of 0.6 – 1.2 which is very much similar to the theoretically specified range (0.75 - 1.25) of the acrylic emulsions. It is observed that the number average diameter of resin-tackified acrylic emulsions(G4-G7) are lower than that of the non-tackified acrylic emulsions(G1-G3).The reason for this typical variation is not clear.

3.5 EFFECT OF PLASTICIZER

BATCH NO.	DOM	DBM	TACK	PEEL	SHEAR
1	-	-	0.6	280	52
2	85	-	1.2	640	36
3	-	85	0.25	150	1.6

Table 3.2 Effect of plasticizer

coating weight vary from 23-25 gsm.

The tack performance of the emulsion polymer depends upon the structure and chain length of the monomer, which affect the glass transition temperature(T_g) of the polymer. Generally low Tg polymer have high tack. Di-Octyl Maleate gives higher tack because of the long chain (presence of octyl group) in comparison of Di Butyl Maleate, which gives very low tack.

3.6 EFFECT OF POLYACRYLIC ACID

BATCH NO.	PAA	DBM	TACK	PEEL	SHEAR
4	400	42.5	0.26	1050	650
5	400	-	0.3	770	500
6	200	-	0.75	650	570
7	100	-	0.8	550	450

Table 3.3 Effect of Poly(acrylic acid)

coating weight from 23-25 gsm

Tack improves with decrease in poly(acrylic acid)concentration (Tg = 106°C) correlates with theory, that, lower the Tg, higher the tack. Peel test defines adhesion and cohesion depending upon adhesive or cohesive failure. In this case, high peel with adhesive failure assists the cohesion. Adhesive failure means, no residue remains on the surface when adhesive with adherend peeled off. The effect of plasticizer can be visualized from high peel and high shear.

3.7 EFFECT OF TACKIFIER

BATCH NO	TACKIFIER RESIN	TACK	PEEL	SHEAR
6	-	0.75	550	570
10	10*	1.66	945	22

Table 3.4 Effect of tackifier

coating weight from 23-25 gsm

* wt.% of monomer

Theoretically,it is known that tackifier resin improves the tack of adhesive. However, it has reverse effect on shear properties of the adhesive. Practically too, we have enhanced tack with reduced shear. This is because of low molecular weight resulting due to introduction of tackifier, which generally contains antioxidants and stabilizer, which are acting as chain transfer agents.

3.8 EFFECT OF TACKIFIER CONCENTRATION

BATCH NO.	TACKIFIER	TACK	PEEL	SHEAR
11	5*	2.0	850	17
12	7.5*	2.0	950	17
13	10*	2.7	650	11

Table 3.5 Effect of tackifier concentration

* wt.% of monomer

coating weight from 23-25 gsm

As the results shows that tack improves with increase in concentration of tackifier resin with a decrease in shear properties. This justifies the theory that at room temperature tackifier resins enhance the tack property at the cost of shear strength.

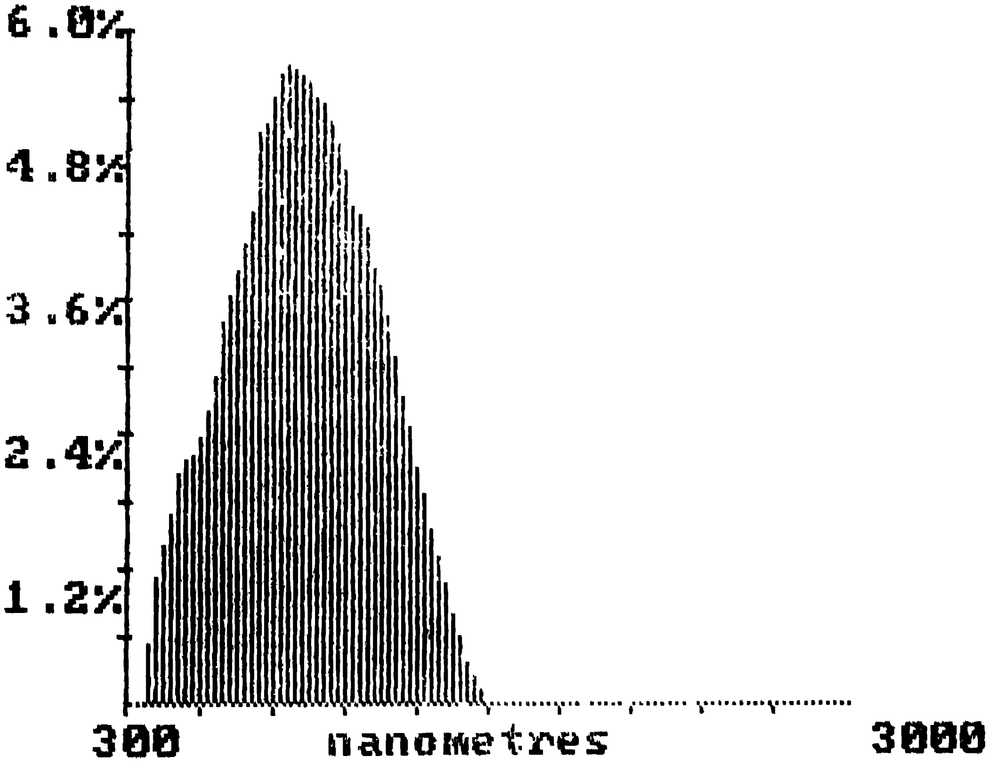
3.9 EFFECT OF MONOMER RATIO WITH TACKIFIER (10%)

BATCH NO.	VAM¶	BA¶	TACK	PEEL	SHEAR
10	30	70	1.66	945	22
13	20	80	2.7	650	11
14	20	80 (AA-1%)*	2.0	900	13

Table 3.6 Effect of monomer ratios

* wt.% of total monomer mixture
¶ wt% of the rest monomer mix.

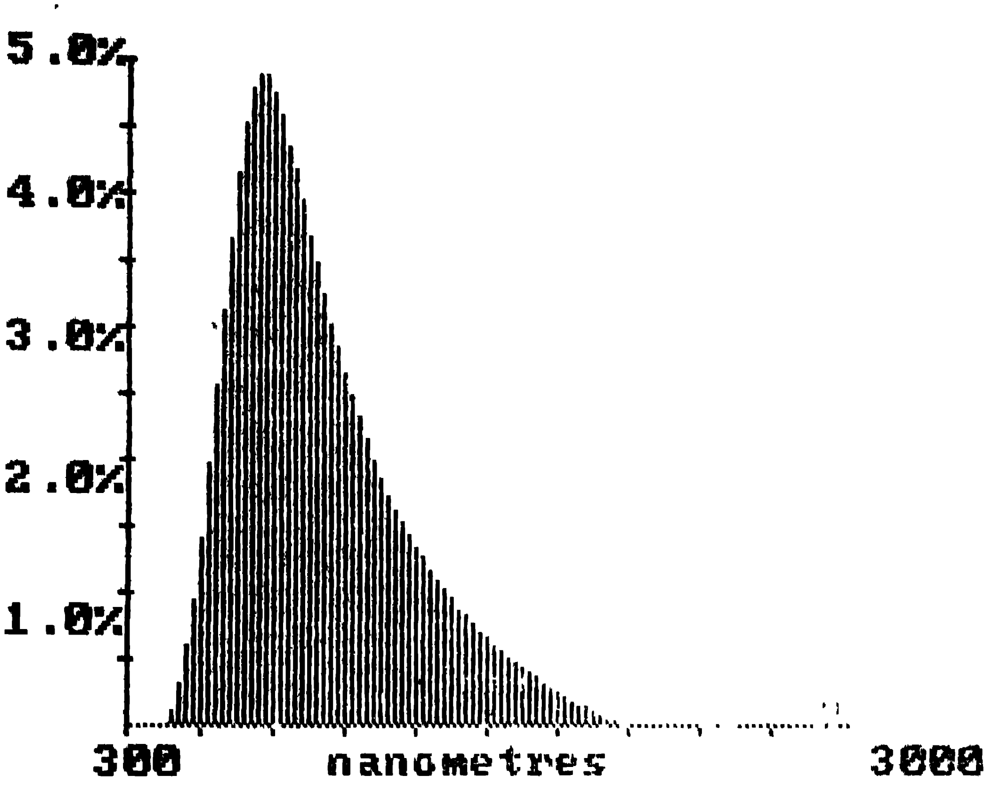
Tack is improved with introduction of tackifier resin with decrease in shear strength. Reduction of monomer (vinyl acetate) with high Tg further improves the tack but also reduces the shear. Addition of acrylic acid improves peel strength but does not have much effect on the shear.



Diameters from 300 to 3000

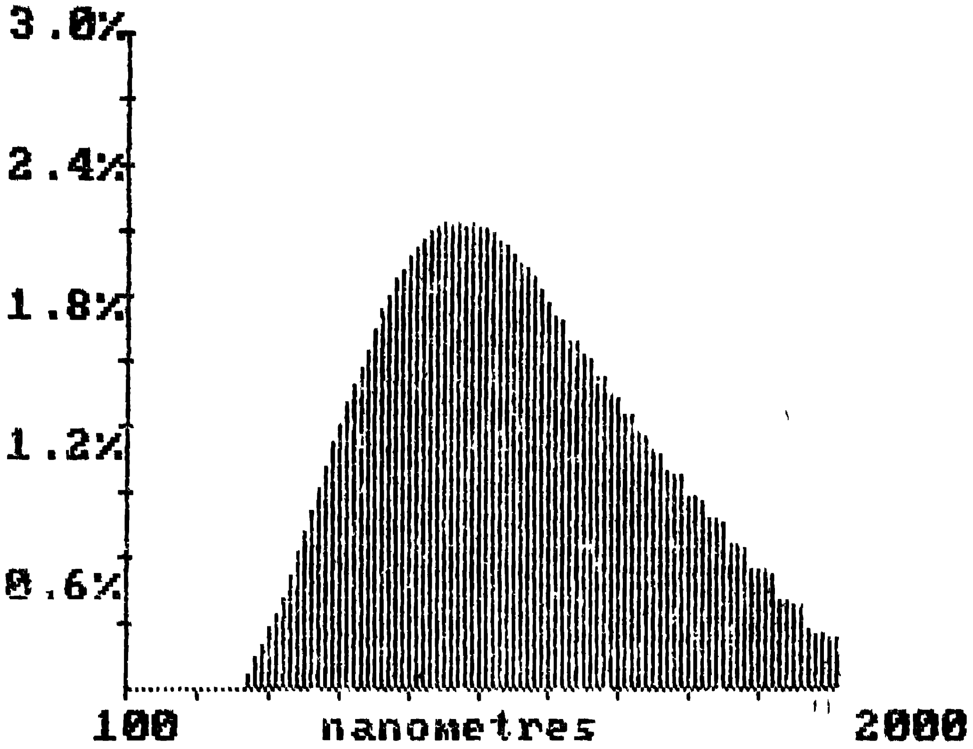
N av D 931.8	N av SD 264.8
S av D 1071.6	W av D 1126 4
Pk D 867	½ Pk 702

G1 – PSD for Batch No - 2



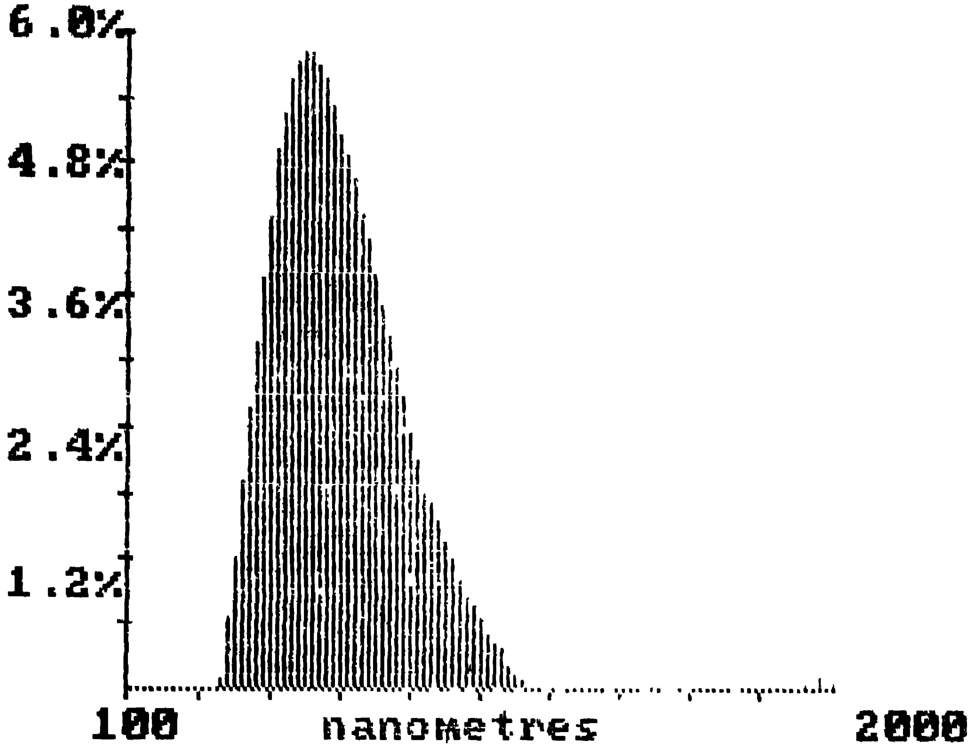
Diameters from 300 to 3000
N av D 978.5 N av SD 313.3
S av D 1187.4 W av D 1296.4
Pk D 759 ½ Pk 540

G2 – PSD for Batch No - 4



Diameters from 100 to 2000
N av D 1126 1 N av SD 349.1
S av D 1333.9 W av D 1421.7
Pk D 955 ½ Pk 912

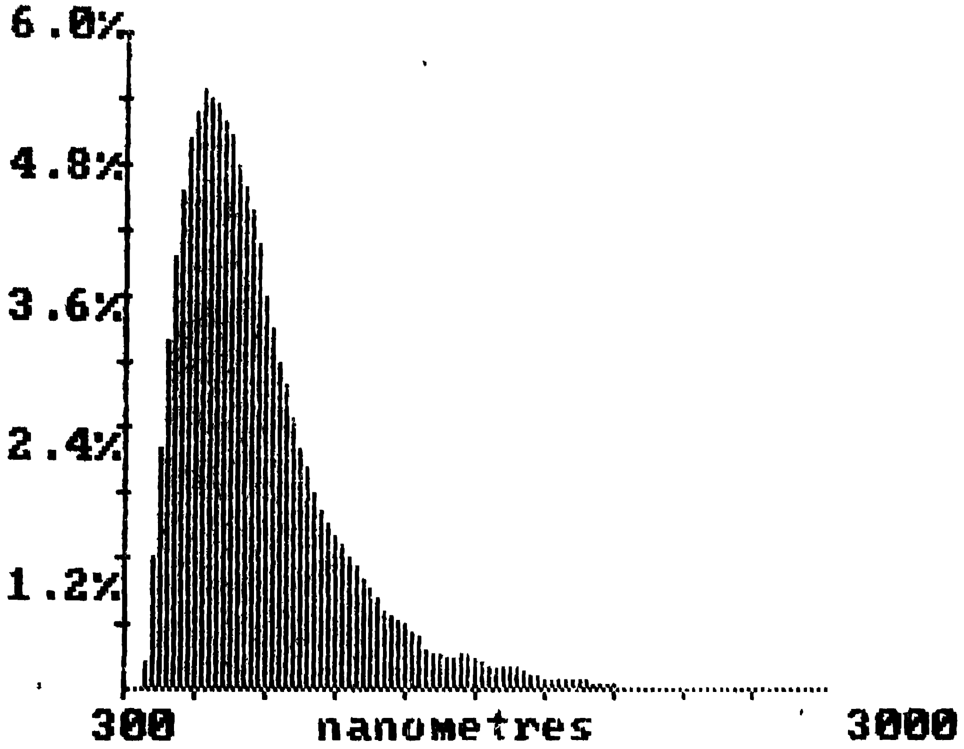
G3 – PSD for Batch No. – 5



Diameters from 100 to 2000

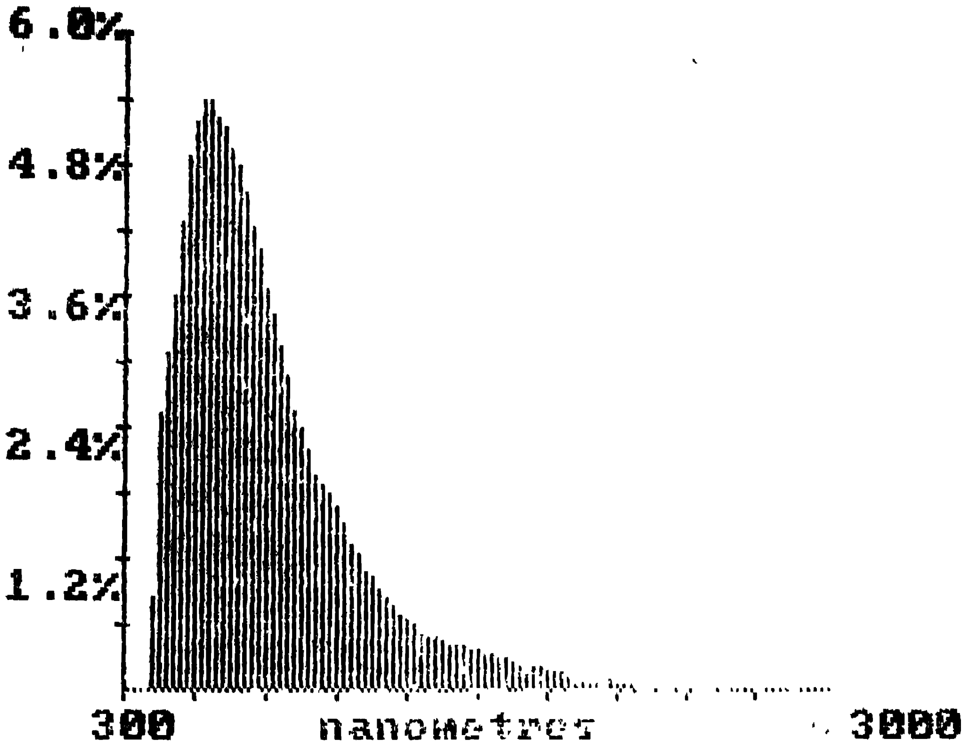
N av D 642.9	N av SD 161 7
S av D 724.4	W av D 764
Pk D 556	½ Pk 399

G4 - PSD for Batch No. -10



Diameters from 300 to 3000
N av D 780 N av SD 298 7
S av D 1033.2 W av D 1186 2
Pk D 570 ½ Pk 486

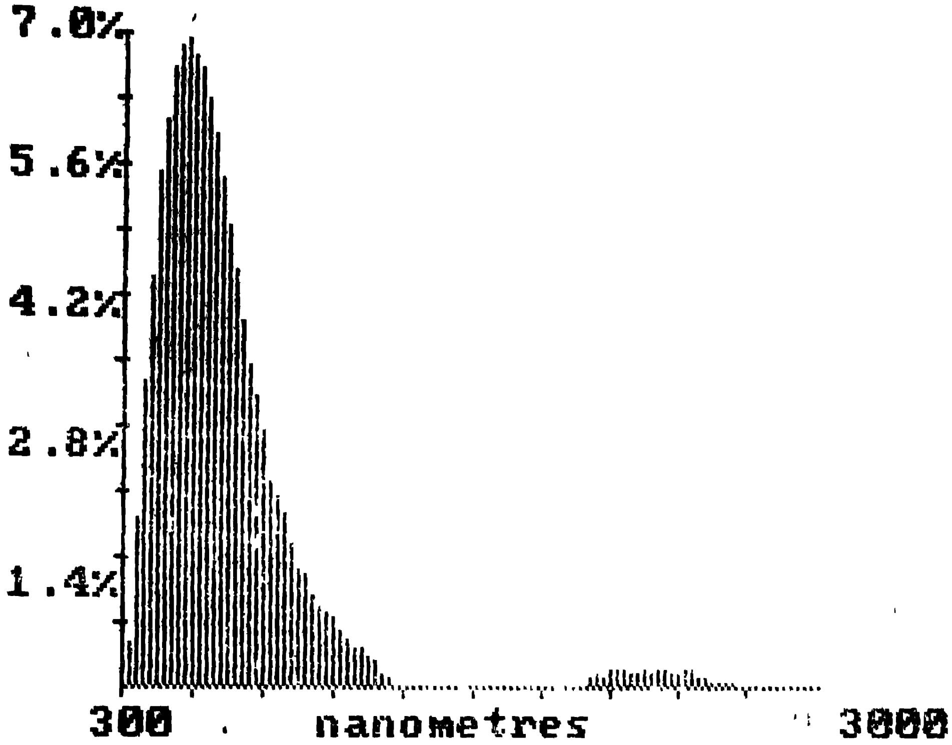
G5 - PSD for Batch No. - 12



Diameters from 300 to 3000

N av D	807.9	N av SD	321.1
S av D	1089	W av D	1253.6
Pk D	597	½ Pk	486

G6 – PSD for Batch No. 13



Diameters from 300 to 3000

N av D	661.2	N av SD	325
S av D	1132.5	W av D	1586.9
Pk D	516	½ Pk	378

G7 – PSD for Batch No. - 14

CONCLUSION

"We are what our thoughts have made us,
so take care about what you think.
Words are secondary,
Thoughts live,
They travel far."
-SWAMI VIVEKANANDA

CONCLUSION

The results shows that poly(acrylic acid) is not compatible with VAM – 2EHA system, while its properties can be improved but formation of large grits is not desirable as it affects the cost of emulsion and makes the application difficult.

VAM – BA system with poly(acrylic acid) gives stable emulsion with desired properties. This system gives high peel and high shear properties with reasonable tack. And is suitable for tape applications.

The VAM – BA system with tackifier gives very high tack and high peel with comparatively low shear. This type of system can be used for the synthesis of permanent labels having good die cuttability and improved wetting characteristics at room temperature.

REFERENCES

1. A.J.Kettleborough, Chapter – 5 in Advances in Adhesives;by D.Brewis and J.comyn.Ed.Warwick Publishing,1983.

2. Andrew Klien & Eric S. Daniels, Chapter 6, in Emulsion Polymerization and Emulsion Polymers, edited by P.A.Lovell & M.S.El-Aasser, John wiley & Sons Ltd.,1997.

3. Bernard, Margaret M.,Tackified Emulsion Pressure Sensitive Adhesive (USP5623011) April 22, 1997.

4. C.W. Benmels, Chapter 47,Pressure sensitive tapes and labels; in Hand book of Adhesives; Irving Skiest; Ed. Van Nostrand – Reinhold Co., New York,1977.

5. D.Satas ,Chapter 5 in Hand book of Pressure Sensitive Adhesive Technology, D. Satas, Ed.Van Nostrand-Reinhold, 1982.

6. D.Satas , Chapter 4, Acrylic adhesives; in Hand book of Pressure Sensitive Adhesive Technology; D.Satas Ed.,Van Nostrand-Reinhoold,1982.

7. D.Satas ,Chapter – 15 in, Hand book of Pressure Sensitive Adhesive Technology, D.Satas Ed., Van Nostrand- Reinhold,1982.

8. G.A. Vandezande, O.W.Smith & D.R. Bassett, Chapter-16, in P.A.Lovell & M.s. El-Aasser, John Wiley & Sons Ltd.,1997.

9. H.Warson, The application of Synthetic Resin Emulsions, Ernest Benn Ltd.,1972.

10. Irving Skiest & Jerry Miron, Chapter-1 in, Hand book of Adhesives; Irving Skeist; Ed. Van Nostrand – Reinhold Co., New York,1977.

11. Istvan Benedek, Development & Manufacture of Pressure Sensitive Products, Marcel Dekker, New York, 1998.

12. Istvan Benedek & Luc J. Heymans,Pressure Sensitive Adhesive Technology, Marcel Dekker, New York, 1997.

13. Jack Dickstein and Robert Bouchard, Manufacture of Plastics.

14. James A. Schlademan, Chapter-20, Hand Book of Pressure Sensitive Adhesive, D. Satas Ed., Van Nostrand-Reinhold,1972.

15. Jacob Lichman, Chapter-44 in, Hand book of Adhesives, Irving Skeist, Ed. Van Nostrand-Reinhold Co., New York, 1997.

16. J. Sheilds, Adhesives Hand book, 3rd Edition ,Butterworth,1984.

17. Knutson, Gaylen M., Adhesive Composition & Method of Preparation, Los Angeles (US-3769151) Oct.30,1973.

18. Knutsen, Gaylen (USP-3661696) !975.

19. Michelle M.Gouthier, for types of Adhesives, in Engineered materials Hand book.Vol 3.

20. Mohamed S.El-Aasser & E.David Sudol, Chapter 2,Emulsion Polymerization and Emulsion Polymers. Edited by P.A.Lovell & M.S. El-Aasser, J.Wiley and Sons Ltd., 1997

21. Robert D.Athey Jr.,Emulsion Polymer Technology, Athey Technologies, California.

22. Robert Y. Lochhead, John A. Davidson & G.M. Thomas, Poly(acrylic acid) thickeners in , Polymers in Aqueous Media by, J.Edward Glass.

23. T. M. Goulding , Pressure sensitive adhesives in, Hand book Of Adhesives.

24. V.R.Gowarikar, N. V. Vishwanathan, Jayadev Shreedhar, Polymer Science, New Age International Ltd.,1996.

25. Yale L. Maltzer, Water Soluble Resins And Polymers, Noyes Data Corporation,1976.

26. Journal of polymer science ,June,1997.

27. Adhesive Technology,June,1998.

"This is not the end,

It is not even the beginning of the end,

But it is the end of the beginning